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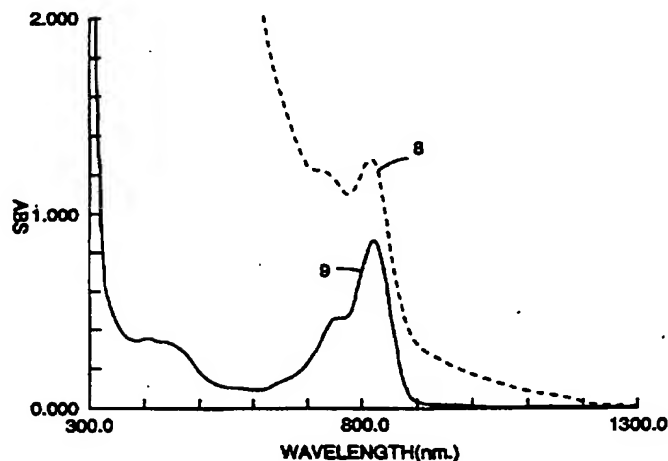
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(54) Title: LASER ADDRESSABLE THERMOGRAPHIC ELEMENTS



(57) Abstract

A thermographic imaging element containing a substrate which is coated on at least one surface thereof with a thermographic imaging system having at least one layer containing light-insensitive organic silver salt; reducing agent for silver ion; a binder; toner; and a dye which absorbs radiation in the wavelength range of about 750-1100 nm. Preferably, there is a layer adjacent to the one containing the light-insensitive organic silver salt, etc., which contains binder and additional dye which absorbs radiation in the range of about 750-1100 nm. When the thermographic imaging element is exposed to radiation of 750-1100 nm of 0.10-2.0 joules/cm<sup>2</sup> for 0.20-200 microseconds, an image density of about 1.0 or greater is formed. When imaging a thermographic imaging element with radiation-absorbing dye in both adjacent layers or only the layer containing binder and dye, the radiation is directed through the layer containing the light-insensitive organic silver salt, etc., before striking the adjacent layer containing radiation-absorbing dye and binder.

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**LASER ADDRESSABLE THERMOGRAPHIC ELEMENTS****Field of the Invention**

The present invention relates to novel  
10 thermographic imaging elements and more particularly,  
it relates to thermographic imaging elements that can  
be directly imaged using an infrared laser diode. The  
present invention further relates to processes for  
imaging the inventive thermographic imaging elements  
15 using an infrared laser diode.

**Background of the Invention**

In the imaging arts, imaging elements that can be  
imagewise exposed by means of light or heat are well  
20 known. Silver halide conventional photographic and  
photothermographic elements are the most representative  
elements of the class of light-sensitive materials. In  
both conventional photographic ("wet silver") and  
photothermographic ("dry silver") elements, exposure of  
25 the silver halide in the photosensitive emulsion to  
light produces small clusters of silver atoms ( $\text{Ag}^0$ ).  
The imagewise distribution of these clusters is known  
in the art as a latent image. Generally, the latent  
image formed is not visible by ordinary means and the  
30 photosensitive emulsion must be further processed in  
order to produce a visible image. In both dry and wet  
silver systems the visible image is produced by the  
reduction of silver ions, which are in catalytic  
proximity to silver halide grains bearing the clusters  
35 of silver atoms, i.e. the latent image. This produces  
a black-and-white image.

Conventional photographic silver halide elements require a wet development process to render the latent image visible. The wet chemistry used in this process requires special handling and disposal of the spent  
5 chemistry. The process equipment is large and requires special plumbing.

In photothermographic elements the photographic silver halide is in catalytic proximity to a non-photosensitive, reducible silver source (e.g., silver  
10 behenate) so that when silver nuclei are generated by light exposure of the silver halide, those nuclei are able to catalyze the reduction of the reducible silver source. The latent image is rendered visible by application of uniform heat across the element.

15 Thermal devices used for developing photothermographic elements address the problems in conventional photographic elements by using a dry process. However, photothermographic elements developed using these devices may have uneven or non-uniform image density,  
20 image distortions, and/or surface abrasion defects. Non-uniform image density defects may occur during the development process due to, for instance, surface variations on the heated member, the presence of foreign matter on the photothermographic element or the  
25 heated member, and insufficient allowance for outgassing of volatile materials generated during development. Image distortions can occur due to uncontrolled dimensional changes in the base of the photothermographic element during heating and/or  
30 cooling of the photothermographic element. Surface abrasions or marring may occur by dragging the photothermographic element across a stationary component in the heating device. In many applications, such as text and line drawings, these defects may be  
35 acceptable. However, users of medical diagnostic, industrial, graphic arts, printed circuit boards, and

other imaging applications desire uniform and high quality images.

U.S. Patent No. 5,041,369 describes a process which capitalizes on the advantages of a dry processed photothermographic element without the need for surface contact with a heating device. The photothermographic element is imagewise exposed with a laser which splits the beam using a second harmonic generation device. In this process, the element is simultaneously exposed with one wavelength of light and thermally activated by the absorption of a light-to-heat near-infrared (NIR) dye at the second wavelength of light. Even though this process has the advantage of simultaneous exposure and heat development of the image, the equipment required is complex and limited by laser outputs capable of generating two useful separate wavelengths. In addition, the photosensitive emulsion still requires both light and heat activation to generate an image.

Photosensitive emulsions which contain silver halide are well known in the art to be capable of causing high minimum density ( $D_{min}$ ), both in the visible and ultraviolet (UV) portions of the spectrum. The high UV  $D_{min}$  is due to the inherent absorption in the near UV of silver halides, particularly silver bromide and silver iodide, and to high haze when silver halide and organic silver salts are present together. High UV  $D_{min}$  is undesirable for graphic arts scanner and imagesetting films since it increases the exposure time required during contact exposure with other media such as UV sensitive printing plates, proofing films, and papers. High haze can also lead to loss of image resolution when imaged photothermographic elements are used as contact films. It is also well known that silver halides in photothermographic elements can lead to poor light stability of the background image density leading to fogging.

A class of imaging elements that do not rely on silver halide-based chemistry is thermographic elements. These materials are widely used in facsimile machines, labels, tickets, charts for recording the output of medical or scientific monitoring apparatus, and the like. In the most common form, the thermographic element comprises a support carrying a coating of a thermally-sensitive composition comprising a color former, usually a substantially colorless electron-donating dye precursor, and a color developer, usually an electron-accepting compound. Heat is imagewise applied to the element by means of a thermal head, a thermal pen or a laser beam, and upon imagewise applied heating, the color former instantaneously reacts with the color developer to form an image. U.S. Patent No. 4,904,572 describes a thermographic element which uses leuco dyes to enhance the developed image. A leuco dye is the reduced form of a color-bearing dye. It is generally colorless or very lightly colored. In this application, silver behenate acts as a Lewis acid which reacts with the leuco dye upon imagewise application of heat to form a colored image. A black image is achieved by the combination of subtractive colors (cyan, yellow, and magenta). It is well known in the art that it is very difficult to achieve a high density neutral tone black using subtractive colors. Since the image is generated by colored dye formation, the absorption of the image in the ultraviolet is weak and therefore, provides little utility as a UV masking film.

Conventional thermographic films typically require imaging dwell times of from 1 to 5 seconds. Processing times of this extent are not practical in a laser imaging application. In order to provide an appropriate imaging dwell time for a laser addressable system, there is a need for a thermographic film

construction which is capable of forming an in-situ image in micro seconds.

Each of the above-mentioned classes of imaging elements has some disadvantage. For example, conventional silver halide photographic materials have a high environmental impact due to the wet processing chemistry; photothermographic materials have lower image fastness, limited optical density, and poor dimensional stability; silver halide-based emulsions typically use visible sensitizers which need to be bleached or removed and need to be handled in the dark or subdued light; both conventional photographic and photothermographic elements require a two-step process (exposure and development); and conventional thermographic elements require high imaging energy, relatively long thermal imaging dwell times, and have lower image fastness and limited UV optical density.

What is needed in the industry are imaging elements and processes which help to overcome the above-disclosed problems. It was against this background that the present inventions were developed.

#### Summary of the Invention

In one embodiment, the present invention provides a thermographic imaging element comprising a substrate having coated on at least one surface thereof a thermographic imaging system comprising at least one layer comprising light-insensitive organic silver salt; reducing agent for silver ion; a binder; toner; and a dye which absorbs radiation in the wavelength range of about 750-1100 nm, wherein the at least one layer comprising the light-insensitive organic silver salt forms an image density of greater than about 1.0 when exposed to 0.10-2.0 joules/cm<sup>2</sup> of radiation (having a wavelength in the range of about 750-1100 nm) in 0.2-200 microseconds.

In another embodiment, the present invention provides a thermographic imaging element comprising a substrate coated with a thermographic imaging system, the thermographic imaging system comprising at least  
5 two adjacent layers, one of the adjacent layers comprising light-insensitive organic silver salt; reducing agent for silver ion; a binder; toner; and optionally, a dye which absorbs radiation having a wavelength in the range of about 750-1100 nm and the  
10 other adjacent layer consisting essentially of dye which absorbs radiation in the wavelength in the range of about 750-1100 nm and binder such that the layer comprising the light-insensitive organic silver salt forms an image density of greater than about 1.0 when  
15 exposed to 0.10 - 2.0 joules/cm<sup>2</sup> of radiation (having a wavelength in the range of about 750-1100 nm) in 0.2 - 200 microseconds.

In a further embodiment, the present invention provides a process for forming an image comprising the  
20 step of exposing a thermographic imaging element comprising a substrate coated with a thermographic imaging system, comprising at least one layer comprising light-insensitive organic silver salt; reducing agent for silver ion; a binder; a dye which  
25 absorbs radiation in the wavelength range of about 750-1100 nm; and toner, to radiation in the range of about 750-1100 nm such that the at least one layer comprising the light-insensitive organic silver salt forms an image density of greater than about 1.0 when exposed to  
30 0.10 - 2.0 joules/cm<sup>2</sup> of radiation in (having a wavelength in the range of about 750-1100 nm) in 0.2 - 200 microseconds.

In still another embodiment, the present invention provides a process for forming an image comprising the  
35 step of exposing a thermographic imaging element comprising a substrate coated with a thermographic



imaging system, the thermographic imaging system comprising at least two adjacent layers, one of the adjacent layers comprising light-insensitive organic silver salt; reducing agent for silver ion; a binder; 5 toner; and optionally, a dye which absorbs radiation having a wavelength in the range of about 750-1100 nm and the other adjacent layer consisting essentially of binder and dye which absorbs radiation having a wavelength in the range of about 750-1100 nm, to 10 radiation having a wavelength range of about 750-1100 nm which is directed to the thermographic imaging element through the layer comprising the light-insensitive organic silver salt before striking the adjacent layer consisting essentially of binder and dye 15 such that the layer comprising the light-insensitive organic silver salt forms an image density of greater than about 1.0 when exposed to 0.10 - 2.0 joules/cm<sup>2</sup> of radiation (having a wavelength in the range of about 750-1100 nm) in 0.2 - 200 microseconds.

20 In a preferred embodiment to the above inventions, an image density of greater than about 2.00 and, more preferably, greater than about 2.50, and most preferably, greater than about 2.75 comprising metallic silver is formed in the layer comprising light- 25 insensitive organic silver salt, reducing agent, etc., upon exposure to 0.10 - 2.0 joules/cm<sup>2</sup> of radiation (having a wavelength in the range of about 750-1100 nm) in 0.2 - 200 microseconds.

The layers ("thermographic silver emulsion 30 layers") comprising light-insensitive organic silver salt, reducing agent for silver ion, etc., in all of the above-disclosed embodiments of the present invention can incorporate up to about 1.0 wt% silver halide, based upon the total weight of the layer.

35 The silver-based thermographic imaging elements and methods for using the thermographic imaging

elements as laser addressable direct-write film provided by the present invention overcome many of the problems seen in current systems. Since the thermographic imaging element is thermally-sensitive, rather than photosensitive, it is white light-handleable and does not require removal of a visible sensitizer. Unlike wet silver and photothermographic elements, no post-processing steps are required for development of the image. When a high power laser diode is scanned across the thermographic imaging element, an in-situ black image is printed out in the thermographic silver emulsion, thus enabling many useful applications such as an on-line inspection system for printed circuit board phototool mask production. In addition, heat shrinkage of the film is minimized since only the imaged portion of the emulsion is heated and the temperature of the substrate is relatively unchanged. This is especially important for applications where registration is critical, such as image-setting films for color reproduction and printed circuit board phototools. In addition, the thermographic imaging element is capable of producing high resolution halftone images which are useful in color reproduction processes.

Other aspects, advantages, and benefits of the present invention are apparent from the detailed description, the examples, the drawings, and the claims.

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#### Brief Description of the Drawings

FIG. 1 shows a schematic representation of a laser sensitometer.

FIG. 2 shows a graph of distance versus the relative intensity of a laser diode comparing the plots for theoretical versus actual profile data for a flat-topped cone shaped laser spot on the film plane.

FIG. 3a shows a graph of the total incident exposure energy plotted against the distance across the laser beam in the cross/scan direction.

FIG. 3b shows a microdensitometer profile of a line imaged with the energy profile depicted in FIG. 3a onto a thermographic element. (Example 16, Sample N not shown.)

FIG. 4 shows a graph of density versus the log of the exposure using the data shown in FIG. 3a.

FIG. 5 shows a graph of absorption versus wavelength comparing the imaged and non-imaged areas of a thermographic imaging element. (Example 16, Sample N not shown.)

#### Detailed Description of the Invention

As used herein, "thermographic imaging element" refers to a substrate coated on at least one surface thereof with a "thermographic imaging system". The thermographic imaging system comprises at least one thermographic silver emulsion layer containing light-insensitive organic silver salt; reducing agent for silver ion; binder; toner; and a dye which absorbs radiation having a wavelength in the range of about 750 - 1100 nm. Additionally, the thermographic imaging system may comprise a layer adjacent to the thermographic silver emulsion layer which contains further radiation-absorbing dye and binder.

In the present invention, the thermographic silver emulsions which are utilized comprise a light-insensitive silver salt; a reducing agent for silver ion; a dye which absorbs radiation having a wavelength in the range of about 750-1100 nm; a toner, binder; and an optional development accelerator.

The light-insensitive silver salts are materials, which in the presence of a reducing agent, undergo reduction at elevated temperatures, e.g., 60°-225°C, to form silver metal. Preferably, these materials are

silver salts of long chain alkanolic acids (also known as long chain aliphatic carboxylic acids or fatty acids) containing 4 to 30 carbon atoms; more preferably, 8 to 28 carbon atoms; and most preferably, 10 to 22 carbon atoms. The latter are also known in the art as "silver soaps".

Non-limiting examples of silver salts of aliphatic carboxylic acids include silver behenate, silver stearate, silver oleate, silver erucate, silver laurate, silver caproate, silver myristate, silver palmitate, silver maleate, silver fumarate, silver tartarate, silver linoleate, silver camphorate, and mixtures thereof. Complexes of organic or inorganic silver salts wherein the ligand has a gross stability constant between 4.0 to 10.0 can also be used. Silver salts of aromatic carboxylic acids and other carboxyl group-containing compounds include silver benzoate, a substituted silver benzoate such as silver 3,5-dihydroxybenzoate, silver o-methylbenzoate, silver m-methylbenzoate, silver p-methylbenzoate, silver 2,4-dichlorobenzoate, silver acetamidobenzoate, silver p-phenyl benzoate, etc., silver gallate, silver tannate, silver phthalate, silver terephthalate, silver salicylate, silver phenylacetate, silver pyromellitate, silver salts of 3-carboxymethyl-4-methyl-4-thiazoline-2-thiones or the like as described in U.S. Pat. No. 3,785,830; and silver salts of aliphatic carboxylic acids containing a thioether group as disclosed in U.S. Pat. No. 3,330,663. Silver salts of compounds containing mercapto or thione groups and derivatives thereof can also be used. Preferred examples of these compounds include silver 3-mercapto-4-phenyl-1,2,4-triazolate, silver 2-mercaptobenzimidazolate, silver 2-mercapto-5-aminothiadiazolate, silver 2-(S-ethylglycolamido)benzothiazolate; silver salts of

thioglycolic acids such as silver salts of *S*-alkyl  
thioglycolic acids (wherein the alkyl group has from 12  
to 22 carbon atoms); silver salts of dithiocarboxylic  
acids such as silver dithioacetate, silver  
5 thioamidoate, silver 1-methyl-2-phenyl-4-thiopyridine-  
5-carboxylate, silver triazinethiolate, silver 2-  
sulfidobenzoxazole; and silver salts as disclosed in  
U.S. Pat. No. 4,123,274. Furthermore, silver salts of  
a compound containing an amino group can be used.  
10 Preferred examples of these compounds include silver  
salts of benzotriazoles, such as silver  
benzotriazolate; silver salts of alkyl-substituted  
benzotriazoles such as silver methylbenzotriazolate,  
etc.; silver salts of halogen-substituted  
15 benzotriazoles such as silver 5-chlorobenzotriazolate,  
etc.; silver salts of carboimidobenzotriazoles, etc.;  
silver salts of 1,2,4-triazoles and 1-*H*-tetrazoles as  
described in U.S. Pat. No. 4,220,709; silver salts of  
imidazoles; and the like. Preferably, the light-  
20 insensitive silver salt material should constitute from  
about 5 to 60% by weight and more preferably, from  
about 30 to 50% by weight, based upon the total weight  
of the thermographic silver emulsion layer.

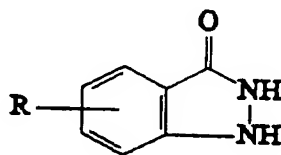
Any reducing agent for silver ion can be used in  
25 the present invention. Such reducing agents are well-  
known to those skilled in the art. Examples of such  
reducing agents include, but are not limited to, methyl  
gallate; hindered phenols; catechol; pyrogallol;  
hydroquinones; substituted-hydroquinones; ascorbic  
30 acid; ascorbic acid derivatives; leuco dyes; and the  
like. The most preferred reducing agents are methyl  
gallate, butyl gallate, and propyl gallate. Whatever  
reducing agent is employed in the present invention is  
preferably used in an amount of about 5.0 to 25.0% by  
35 weight and more preferably, from about 10.0 to 20.0% by

weight, based upon the total weight of the thermographic silver emulsion layer.

Toners are also used in the thermographic silver emulsion layer(s). Examples of toners include  
5 phthalazinone, phthalazine, barbituric acid, succinimide, and phthalimide. Combination of toners have been found to be especially useful, the preferred combinations being phthalazinone with barbituric acid and phthalimide with barbituric acid and most preferred  
10 being succinimide with barbituric acid. The toner(s) should preferably be present in an amount in the range of about 0.2 to 10.0% by weight; more preferably, about 1.0 to 8.0% by weight; and most preferably, about 2.0 to 6.0% by weight, based upon the total weight of the  
15 thermographic silver emulsion layer.

Auxiliary reducing agents or development accelerators may be optionally included in the thermographic silver emulsion layer depending upon the silver source used. Preferably, the auxiliary reducing  
20 agent comprises a 3-indazolinone or urea compound as a development accelerator.

3-indazolinone compounds used in the present invention preferably have the following structure:



30 wherein R is selected from the group consisting of: hydrogen; an alkyl group of 1 to 4 carbon atoms; halogen; -COOH and -R<sup>1</sup>COOH wherein R<sup>1</sup> is an alkyl group having from 1 to 4 carbon atoms. Preferably, R is  
35 hydrogen or an alkyl group having from 1 to 4 carbon atoms and most preferably, R is hydrogen.

Such 3-indazolinone compounds can be synthesized according to procedures well known to those skilled in the art of synthetic organic chemistry. Alternatively, such materials are commercially available, such as from  
5 Aldrich Chemical Company of Milwaukee, Wisconsin; Lancaster Chemical Company of Windham, New Hampshire; and K&K Laboratories of Cleveland, Ohio.

As is well understood in this area, a large degree of substitution is not only tolerated, but is often  
10 advisable. Thus, as used herein the phrase "group" is intended to include not only pure hydrocarbon substituents such as methyl, ethyl, and the like, but also such hydrocarbon substituents bearing conventional substituents in the art such as hydroxy, alkoxy,  
15 phenyl, halo (F, Cl, Br, I), cyano, nitro, amino, etc.

Urea compounds used in the present invention preferably have the following formula:



wherein  $\text{R}^2$  and  $\text{R}^3$  each independently represent hydrogen; a  $\text{C}_1\text{-C}_{10}$  alkyl or cycloalkyl group; or phenyl; or  $\text{R}^2$  and  $\text{R}^3$  together form a heterocyclic group  
25 containing up to 6 ring atoms. Preferably,  $\text{R}^2$  and  $\text{R}^3$  represent hydrogen; a  $\text{C}_1$  to  $\text{C}_5$  alkyl or cycloalkyl group; or phenyl; or  $\text{R}^2$  and  $\text{R}^3$  together form a heterocyclic group containing up to 5 ring atoms. Such urea compounds can be readily synthesized and are  
30 commercially available. Non-limiting examples of such urea compounds include urea; 1,3-diphenyl urea; 1,3-diethyl urea; butyl urea; and 2-imidazolidone. The most preferred development accelerator is 2-imidazolidone.

35 The thermographic imaging elements of the present invention are not light-sensitive in the traditional sense and therefore, do not need to contain photosensitive agents such as silver halides;

photoinitiator; or photogenerated bleaching agents. The thermographic silver emulsion layers can have less than 1%, less than 0.75%, less than 0.5%, or 0% by weight, based upon the total weight of the

5 thermographic silver emulsion, and perform well. The silver halide is deemed to be ineffective if it does not catalyze formation of a latent image.

Light stabilizers such as benzotriazole, phenylmercaptotetrazole, and other light stabilizers  
10 known in the art may be added to the thermographic silver emulsion. The preferred light stabilizer is benzotriazole. The light stabilizer should preferably be present in an amount in the range of about 0.1% to 3.0% by weight of the thermographic silver emulsion  
15 layer and more preferably, from 0.3 to 2.0 wt%.

The thermographic silver emulsion layer utilized in the present invention also employs a binder. Any conventional polymeric binder known to those skilled in the art can be utilized. For example, the binder may  
20 be selected from any of the well-known natural and synthetic resins such as gelatin, polyvinyl acetals, polyvinyl chloride, cellulose acetate, polyolefins, polyesters, polystyrene, polyacrylonitrile, polycarbonates, and the like. Copolymers and  
25 terpolymers are, of course, included in these definitions, examples of which, include, but are not limited to, the polyvinyl aldehydes, such as polyvinyl acetals, polyvinyl butyrals, polyvinyl formals, and vinyl copolymers. Preferably, the binder should be  
30 present in an amount in the range of 10 to 60% by weight and more preferably, 15 to 50% by weight, based upon the total weight of the thermographic silver emulsion layer.

The thermographic element of the present invention  
35 employs a dye which absorbs electromagnetic radiation having a wavelength in the range of between about 750-



1100 nm, preferably in the range of about 750-900 nm, and most preferably, in the range of about 750-870 nm.

The dye should be soluble in the coating solvent, preferably ketones or aromatic solvents, such as methyl ethyl ketone or toluene. The dye should also be miscible with the binder and compatible with the silver salts, activators, and developers used in the emulsion. For use in UV (ultraviolet) contact film or mask applications the optical density of the dye is preferably greater than 1.0 optical density units with a concomitant weak absorption of less than 0.2 optical density units in the UV region corresponding to the wavelength of exposure devices for which the material will be used as a mask (250-450 nm). The optical density is measured using a MacBeth Model TD523 densitometer equipped with a status 18A filter. It is also desirable, but not necessary, for the dye to have a low visible background absorption.

The radiation-absorbing dye can be employed in the same layer as the light-insensitive organic silver salt; reducing agent for silver ion; toner; and binder. Alternatively, the dye can be employed in the foregoing layer as well as in an adjacent layer or primarily in the adjacent layer. The radiation-absorbing dye may be added directly to the thermographic silver emulsion layer or indirectly by allowing the dye to migrate from the adjacent layer, containing the dye, into the thermographic silver emulsion layer during the manufacturing process of the thermographic imaging element.

Suitable dyes include, but are not limited to, oxonol, squarylium, chalcogenopyrylarylidene, bis(chalcogenopyrylo)polymethine, bis(aminoaryl)polymethine, merocyanine, trinuclear cyanine, indene-bridged polymethine, oxyindolizine, ferrous complex, quinoid, nickel dithiolene complex,

and cyanine dyes such as carb cyanin , azacarbocyanine, hemicyanine, styryl, diazacarbocyanine, triazacarbocyanine, diazahemicyanine, polymethinecyanine, azapolymethinecyanine, holopolar, 5 indocyanine, and diazahemicyanine dyes.

The amount of dye present in the thermographic imaging element will be dependent upon whether the dye is incorporated solely into the thermographic silver emulsion layer or in an adjacent layer as well. When 10 the dye is present solely in the thermographic silver emulsion layer, the dye will be present in an amount of from 0.10-5.0 wt% and preferably from 0.2 - 3.0 wt%, based upon the total weight of the thermographic silver emulsion layer.

15 When present in an adjacent layer, the dye will be present in the thermographic silver emulsion layer in an amount of from 0 - 5.0 wt% and preferably, from about 0 - 1.0 wt%, based on the total weight of the thermographic silver emulsion layer. In the adjacent 20 layer containing dye and binder, the dye will be present in an amount of from 1-25 wt% and preferably, 5 - 20 wt%, based upon the total weight of the adjacent layer.

Any suitable base or substrate material known to 25 those skilled in the art can be used in the present invention. Such materials can be opaque, translucent, or transparent. Commonly employed base or substrate materials utilized in the thermographic arts include, but are not limited to, paper; opaque or transparent 30 polyester and polycarbonate films; and specularly light reflective metallic substrates such as silver, gold, and aluminum. As used herein, the phrase "specularly light reflecting metallic substrates" refers to metallic substrates, which when struck with light, 35 reflect the light at a particular angle as opposed to reflecting the light across a range of angles.

Optionally, a protective or anti-stick layer, positioned on top of the thermographic imaging element, may be used. Any conventional anti-stick material may be employed in the present invention. Examples of such anti-stick materials, include, but are not limited to waxes, silica particles, styrene-containing elastomeric block copolymers such as styrene-butadiene-styrene, styrene-isoprene-styrene, and blends thereof with such materials as cellulose acetate, cellulose acetate butyrate, cellulose acetate propionate, and poly(vinyl butyral).

Additional layers may be incorporated into the thermographic elements of the present invention such as a primer layer or anti-static layer. Furthermore, an anti-static or anti-stick layer may optionally be applied to the back of the support. Materials for such purposes are well known to those skilled in the art.

The thermographic imaging system, anti-stick, infrared or near-infrared dye absorbing, and anti-static layers employed in the present invention can be applied by any conventional method such as knife coating, roll coating, dip coating, curtain coating, hopper coating, etc. If desired, two or more layers may be coated simultaneously by the procedures described in U.S. Patent No. 2,761,791 and British Patent No. 837,095.

The thermographic imaging elements of the present invention are imaged by exposure to infrared or near-infrared laser radiation, typically from a infrared or near-infrared laser diode. As is well known in the thermal imaging arts, infrared or near-infrared laser diodes may be advantageously arranged in an array to increase imaging speed. Lasers that can be used to provide infrared or near-infrared radiation include substantially any laser capable of generating light in the infrared and near-infrared region of the

electromagnetic spectrum from about 750 to 1100 nm, including dye lasers; solid state diode lasers such as aluminum gallium arsenide diode lasers that emit in the region of 780 to 870 nm; and diode-pumped solid state lasers such as Nd:YAG, Nd:YLF, or Nd:glass.

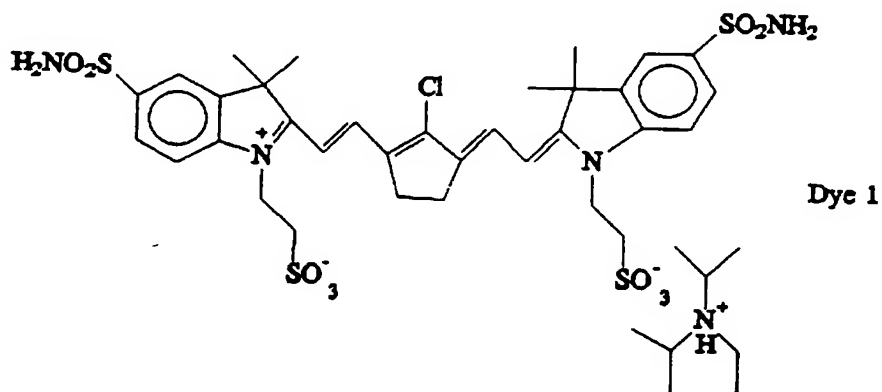
The following non-limiting examples further illustrate the present invention.

#### EXAMPLES

Materials used in the following examples are available from standard commercial sources such as Aldrich Chemical Co. (Milwaukee, WI) unless otherwise specified.

Silver behenate and silver laurate homogenates may be prepared as disclosed in U.S. Pat. No. 4,210,717 (column 2, lines 55-57) or U.S. Pat. No. 3,457,075 (column 4, lines 23-45 and column 6, lines 37-44).

The following dyes were used in various examples which follow:

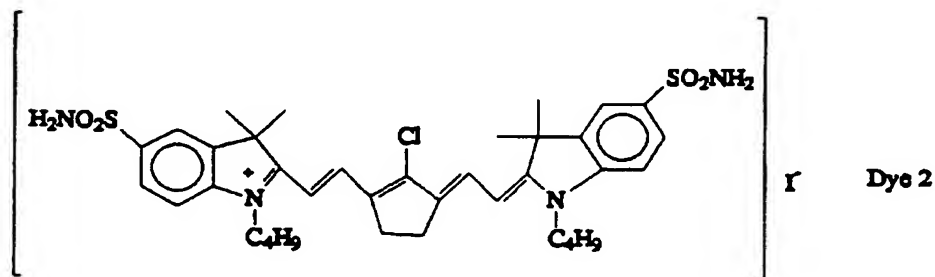


20

Preparation of Dye 1: 5-Sulfamoyl-2,3,3-trimethylindolenine was prepared according to the

method described in U.S. Patent No. 4,062,682. A mixture of 37.0g of 5-sulfamoyl-2,3,3-trimethylindolenine, 16.7mL of 2-chloroethanesulfonyl chloride, and 200mL of acetonitrile were refluxed for 6 hours. After the addition of 18.5mL of water, the mixture was stirred overnight. The separated solid was filtered, washed with acetonitrile, and dried to give 11.0g of a 1-sulfoalkylated quaternary salt intermediate.

- 10 A mixture of 6.5g of chlorocyclopentene dialdehyde, 26g of the quaternary salt intermediate prepared above, 108mL of acetic anhydride, and 72mL of acetic acid was stirred for 10 minutes at room temperature. After addition of 12.8mL of
- 15 diisopropylethylamine, the mixture was stirred overnight. The separated solid was filtered, washed with the solvent mixture, and dried to give 20.0g of dye 1.



20

- Preparation of Dye 2: In a 3L flask, 385g of trimethyl sulphonamido indolenine was added with 250mL of butyronitrile. To this mixture was added, with no
- 25 exotherm, 225mL (364g) of butyliodide followed by 750mL of additional butyronitrile. The mixture was heated to reflux with efficient overhead stirring for 22.5 hours. The heat was removed and the mixture allowed to cool to

about 40 C. Stirring was continued for 1 hour, after the addition of 1L of ethylacetate. The solid was filtered, washed with ethylacetate, and dried to give 595.6g of N-butyl-2,3,3-trimethyl-5-sulphonamido  
5 indoleninium iodide.

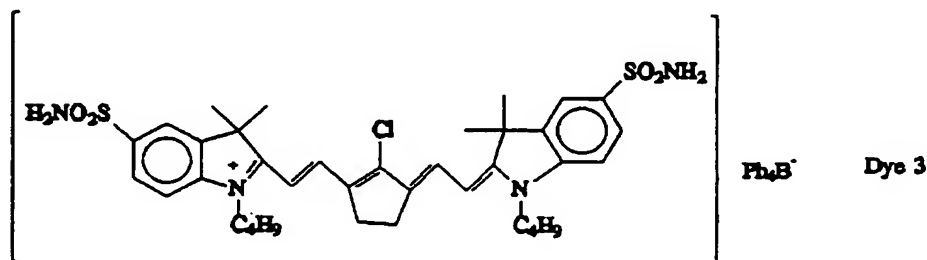
To a solution of 370mL of methylene chloride and 558mL of dimethylformamide, cooled to below 5°C, was added dropwise over 1 hour 277mL of phosphorus oxychloride at a rate such that the temperature did not  
10 exceed 5°C. After the completion of the addition, the external cooling was removed and the mixture was stirred for 1 hour. Over a 30 minute period, 75mL of cyclopentanone was added in two portions. After the first addition, a slow increase in temperature and  
15 color was observed to about 35°C, at which time the second portion was added resulting in a large exotherm. After the exotherm subsided, the mixture was heated to reflux for 4 hours. The mixture was distilled under a slight vacuum after the addition of 1L of ethylacetate.  
20 Approximately 250mL of liquid was collected to which 700mL of ethylacetate was added when a precipitate started to form. The mixture was stirred overnight. The solid was filtered, washed with 1L of ethylacetate, followed by heptane, and dried under vacuum at 35°C for  
25 4 hours giving rise to 115.8g of crude chlorocyclopentene dialdehyde.

The crude chlorocyclopentene dialdehyde was dissolved in 1250 mL of water. Crystals started to appear after about 1 hour. The mixture was allowed to  
30 stand over the weekend. The brownish solid was filtered, washed with water, and dried under vacuum at 35°C for 7 hours giving rise to 61.0g of chlorocyclopentene dialdehyde.

To a solution of 450mL of acetic acid and 450mL of  
35 acetic anhydride was added 278.7g of N-butyl-2,3,3-trimethyl-5-sulphonamide indoleninium iodide and 47.6g

f cyclopentene dialdehyde. To the stirred mixture was added dr pwise 90mL f triethylamine over 5 minutes at 60-65°C. No large exotherm was observed. The mixture was heated for an additional 30 minutes, after which  
 5 the heat was removed and the reaction mixture cooled to 15°C. The resultant golden-brown solid was filtered and washed with a 1:1 mixture of acetic acid:acetic anhydride until the washings were greenish rather than purple. Residual acetic acid and acetic anhydride were  
 10 removed by suspending the solid in 1L of ethyl acetate, followed by stirring for 90 minutes. The solid was filtered and washed with ethyl acetate. The filtrate had a pink hue. The solid was dried at 45°C under vacuum overnight giving rise to 250.0g of Dye 2.

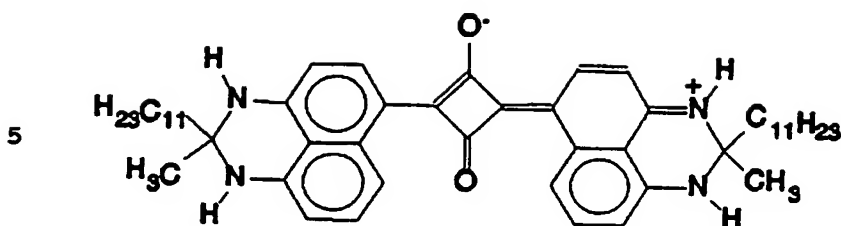
15



Preparation of Dye 3: A mixture of 0.1 moles of Dye 2  
 20 prepared above, 0.1 moles of sodium tetraphenylborate, and 500mL of methanol was refluxed with stirring for 10 minutes. The solid was filtered, washed with methanol, followed by water, and then dried to give 0.97 moles of Dye 3.

25

Dye 4



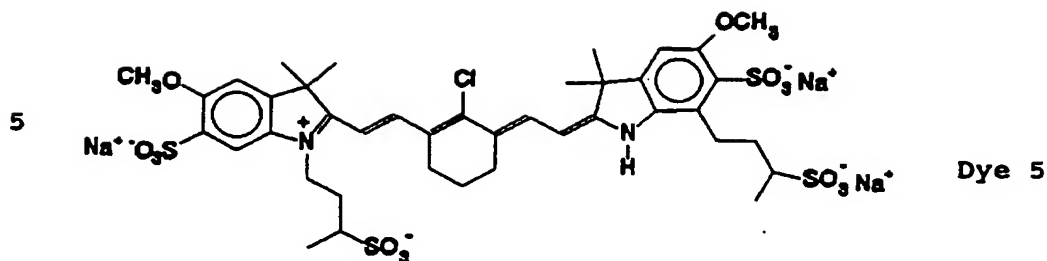
10

Preparation of Dye 4: A stirred mixture of 26.05g of 1,8-diaminonaphthalene, 32.66g of 2-tridecanone, 55mg of *p*-toluenesulfonic acid monohydrate, and 250mL of toluene was heated to reflux under a nitrogen atmosphere using a Dean-Stark trap to remove the water evolved from the reaction for 5 hours. The mixture was then washed with saturated sodium bicarbonate solution, dried over anhydrous potassium carbonate, filtered, and the solvent removed under reduced pressure. The product was distilled to yield 48.86g of dihydroperimidine intermediate; b.p. 192-213°C at 0.3 to 0.4 torr.

A stirred mixture of 8.0g of the dihydroperimidine intermediate prepared above, 1.48g of squaric acid, 64mL of *n*-butanol, and 64mL of toluene was heated to reflux under a nitrogen atmosphere using a Dean-Stark trap to remove the water evolved from the reaction for 3 hours. The mixture was filtered, poured into 600mL of petroleum ether (b.p. 35-60°C), and kept at 5°C for 18 hours. The product was filtered off, washed with petroleum ether, and air dried to give 6.45g of Dye 4.

35





10

15 Preparation of Dye 5: With stirring, 28g of 2,3,3-trimethyl-5-methoxyindolenine was added to 80mL of fuming sulfuric acid (10% of SO<sub>3</sub>). The mixture was stirred overnight at room temperature and then poured onto 500g of crushed ice. The aqueous solution was

20 neutralized with a 30% sodium hydroxide solution and evaporated to dryness under vacuum. The residue was extracted with methanol and the solution evaporated. The solid was picked up in ethanol, filtered, washed with ethanol and dried under vacuum to give 20g of an

25 indolenine sulfate salt intermediate as yellowish prisms.

A mixture of 20g of the indolenine sulfate salt intermediate prepared above, 20g of 2,4-butanediyl sulfone, and 80mL of benzonitrile was refluxed with stirring for

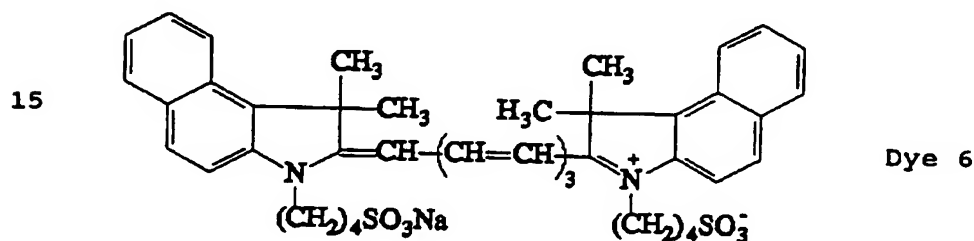
30 5 hours. The solid formed was filtered, washed with ethylacetate, and dried under vacuum to give 25g of a sulfonalkylated quaternary salt intermediate as light-brown prisms.

A mixture of 14.2g of the sulfonalkylated

35 quaternary salt intermediate prepared above, 7.5g of N-(2-chloro-3-(dimethylamino)methylene)-1-cyclohexen-1-

yl)methylene)-N-methylmethanaminium chloride (prepared as described in EPO Application No. 0288261), 5.4mL of dicyclohexylethylamine, and 75mL of benzonitrile was stirred at room temperature overnight. The mixture was  
 5 filtered and the filtrate added to ethylacetate. The solid was filtered and dried. The solid was dissolved in 50mL of ethanol and 3g of sodium iodide added. The precipitate was filtered, washed with acetonitrile, and dried to give 3g of Dye 5 as green prisms.

10



20

Dye 6 is commercially available from Eastman Kodak Co., Rochester, NY.

25

#### Examples 1-3

The following coating solutions were used in the preparation of Examples 1-3:

#### Silver Emulsion:

30 Silver behenate homogenate 160g  
 (10% by weight in methyl ethyl ketone)

Butvar<sup>™</sup> B76 poly(vinyl butyral), available from 20g  
 Monsanto Co.

35

#### Thermographic Coating Solutions:

The thermographic coating solutions for Examples 1-3 were prepared by mixing the following ingredients with 20g of the silver emulsion described above:

5	Material	Example 1	Example 2	Example 3
	Methyl Gallate	0.6g	0.6g	0.6g
	Pyrogallol	0.2g	0.2g	0.2g
	Phthalazinone	0.2g	0.2g	0.2g
	Succinimide	0.1g	0.1g	0.1g
10	2-imidazolidone	0.1g	0.1g	0.1g
	Barbituric acid		0.05g	0.05g
	Benzotriazole			0.02g

Each of the solutions were coated onto a 0.08mm (3  
15 mils) polyester substrate at a 0.1mm (4 mils) wet thickness and air dried at 60°C for 3 minutes.

An infrared-absorbing topcoat solution was prepared by mixing 0.08g of Dye 1, 1.0g of CA 398-6 cellulose acetate resin, and 20.0g MEK. The topcoat  
20 solution was coated onto the thermographic layer at a 0.05mm (2 mils) wet thickness and air dried for 3 minutes at 60°C.

#### Examples 4-6

25 The following coating solutions were used in the preparation of Examples 4-6:

#### Silver Emulsion:

30	Silver laurate full soap homogenate (10% by weight in methyl ethyl ketone)	160g
	BX-1 poly(vinyl butyral), available from Sekisui Chemical Co.	10g

#### 35 Thermographic Coating Solutions:

The therm graphic coating solutions for Examples 4-6 were prepared by mixing the following ingredients with 20g of the silver emulsion described above:

5

Material	Example 4	Example 5	Example 6
Methyl Gallate	0.6g	0.6g	0.6g
Pyrogallol	0.2g	0.2g	0.2g
Phthalazinone	0.2g	0.2g	0.2g
10 Succinimide	0.1g	0.1g	0.1g
2-imidazolidone	0.1g	0.1g	0.1g
Barbituric acid		0.05g	0.05g
Benzotriazole			0.02g

15 Each of the solutions were coated onto a 0.08mm (3 mils) polyester substrate at a 0.1mm (4 mils) wet thickness and air dried at 60°C for 3 minutes.

An infrared-absorbing topcoat solution was prepared by mixing 0.08g of Dye 1, 1.0g of CA 398-6  
 20 cellulose acetate resin, and 20.0g MEK. The topcoat solution was coated onto the thermographic layer at a 0.05mm (2 mils) wet thickness and air dried for 3 minutes at 60°C.

Table 1 summarizes the results of exposing the  
 25 materials of Examples 1-6 with a 810 nanometer laser diode (available from Spectra Diode Labs of San Jose, CA) at 1.75 J/cm<sup>2</sup> focused on the film plane at (a 7 micron spot size). The visible optical densities were measured using a Perkin Elmer microdensitometer PDS  
 30 1010M and the UV optical densities were measured using a MacBeth TD523 densitometer equipped with a status 18A filter. The UV light stability was determined by

allowing the sample to stand in a fluorescent (1,000 foot candles, 90 F) light box for 24 hours.

5

Table 1

Example	1	2	3	4	5	6
Visible Dmax	3.06	3.23	3.25	3.87	3.84	3.83
Visible Dmin	0.05	0.05	0.05	0.07	0.07	0.07
UV Dmin	0.15	0.14	0.13	0.19	0.15	0.16
UV Dmin 24hr stability	0.55	0.61	0.23	0.53	0.59	0.25

Examples 3 and 6 clearly show a significant improvement in UV Dmin light stability when benzotriazole is added to the thermographic silver emulsion.

20

Example 7

The following coating solutions were used in the preparation of Example 7:

Silver Emulsion:

25 Silver behenate homogenate  
(10% by weight in methyl ethyl ketone) 160g

BX-1 poly(vinyl butyral), available from Sekisui  
Chemical Co. 10g

30

Thermographic Coating Solution:

The thermographic coating solution was prepared by adding 20g of the silver emulsion to 0.6g of methyl gallate, 0.1g of succinimide, 0.1g phthalimide, 0.1g tetrachlorophthalic anhydride, 0.02g of benzotriazole, 0.05g of barbituric acid with 4mL of methanol, and 1mL

of MEK. The solution was coated onto a 0.08mm (3 mils) polyester substrate at a 0.08mm (3 mils) wet thickness and air dried at 60°C for 3 minutes.

An infrared-absorbing topcoat solution was prepared by mixing 0.08g of Dye 1, 0.5g of Sekisui BX-1 poly(vinyl butyral), and 20.0g MEK. The topcoat solution was coated onto the thermographic layer at a 0.05mm (2 mils) wet thickness and air dried for 3 minutes at 60°C.

Example 7 was exposed with a 810 nanometer laser diode (available from Spectra Diode Labs of San Jose, CA) at 1.75 J/cm<sup>2</sup> focused on the film plane at (a 7 micron spot size). The imaged film gave rise to a visible Dmax of 3.4, visible Dmin of 0.08, UV Dmax of 3.6 and UV Dmin of 0.17. The visible optical densities were measured using a Perkin Elmer microdensitometer PDS 1010M. The UV optical densities were measured using a MacBeth Model TD523 densitometer equipped with a status 18A filter.

20

#### Example 8

The following coating solutions were used in the preparation of Example 8:

#### 25 Silver Emulsion:

Silver behenate homogenate (10% by weight in methyl ethyl ketone)	160g
BX-1 poly(vinyl butyral), available from Sekisui Chemical Co.	15g
30 Acryloid™ A-21 acrylic resin, available from Rohm and Haas	6g
Methyl ethyl ketone (MEK)	50g

#### 35 Thermographic Coating Solution:

The thermographic coating solution was prepared by adding 15g of the silver emulsion to 0.6g of methyl

gallate, 0.1g phthalazinone, 0.1g 2-imidazolidone, 0.1g tetrachlorophthalic anhydride, 0.05g of barbituric acid with 4mL of methanol, 1mL of MEK, and 1mL of tetrahydrofuran. Before coating, 0.13g of Dye 1 was  
5 added to the solution. The solution was coated onto a 0.08mm (3 mils) polyester substrate at a 0.08mm (3 mils) wet thickness and air dried at 50°C for 3 minutes.

A topcoat solution containing a 2.4% by weight  
10 solution of BX-1 poly(vinyl butyral) was overcoated onto the thermographic layer at a 0.05mm (2 mil) wet thickness and air dried at 50°C for 3 minutes.

#### Examples 9-10

15 The following coating solutions were used in the preparation of Examples 9-10:

#### Silver Emulsion:

20	Silver behenate homogenate	160g
	(10% by weight in methyl ethyl ketone)	
	BX-1 Poly(vinyl butyral), available from	5g
	Sekisui Chemical Co.	

#### 25 Thermographic Coating Solution:

The thermographic coating solutions were prepared by adding 15g of the silver emulsion to 0.6g of methyl gallate, 0.1g of succinimide, 0.1g of 2-imidazolidone, 0.1g of tetrachlorophthalic anhydride, 0.05g of  
30 barbituric acid with 4mL of methanol, and 1mL of MEK. Before coating, 0.08g of Dye 2 was added to the solution in Example 2 and 0.08g of Dye 3 was added to the solution in Example 3. The solution was coated onto a 0.08mm (3 mils) polyester substrate at a 0.08mm  
35 (3 mils) wet thickness and air dried at 50°C for 3 minutes.

A topcoat solution containing a 2.4% by weight solution of BX-1 poly(vinyl butyral) was overcoated

onto the thermographic layer at a 0.05mm (2 mils) wet thickness and air dried at 50°C for 3 minutes.

Examples 11-12

- 5 The following coating solutions were used in preparation of Examples 11-12:

Silver Emulsion:

10	Silver behenate homogenate (10% by weight in methyl ethyl ketone)	160g
	Butvar™ B-76 poly(vinyl butyral)	20g

Thermographic Coating Solution:

- 15 The thermographic coating solution was prepared by adding 15g of the silver emulsion to 0.8g of methyl gallate, 0.2g of succinimide, 0.1g of phthalazinone, 0.1g of 2-imidazolidone in 4mL of methanol, and 1mL of methyl ethyl ketone. Before coating, 0.05g of Dye 4
- 20 was added to the solution in Example 11 and 0.08g of Dye 5 was added to the solution in Example 12. The solutions were coated onto a .08mm (3 mils) polyester substrate at a 0.1mm (4 mils) wet thickness and air dried at 21°C for 10 minutes.
- 25 A topcoat solution containing a 2.4% by weight solution of CA398-6 cellulose acetate, available from Eastman Kodak Co., was overcoated onto the thermographic layer at a 0.05mm (2 mils) wet thickness and air dried at 21°C for 20 minutes.
- 30 Table 2 summarizes the results of exposing the materials of Examples 8-12 with a 810 nanometer laser diode (available from Spectra Diode Labs of San Jose, CA) at 1.75 J/cm<sup>2</sup> focused on the film plane at (a 7 micron spot size). Maximum (D<sub>max</sub>) and minimum (D<sub>min</sub>)
- 35 optical densities were measured using a MacBeth Model TD523 densitometer equipped with a status 18A filter.



Table 2

	Example #	8	9	10	11	12
	Exposure time (microseconds)	72	45	45	45	72
5	D <sub>max</sub>	3.2	3.0	1.55	2.5	3.1
	UV D <sub>min</sub>	0.19	0.16	0.13	0.18	0.18
	Visible D <sub>min</sub>	0.07	0.07	0.07	0.07	0.13

10

Example 13

To show the effect of having halide ion present in the thermographic silver emulsion, 0.2g of calcium bromide was added to the thermographic coating solution of Example 9. The thermographic layer turned totally  
 15 black when air dried at 21°C for 3 minutes.

Example 14

The following coating solutions were used in the preparation of Example 14:

20 Silver Emulsion:

Silver behenate homogenate	160g
(10% by weight in methyl ethyl ketone)	
Butvar™ B-76 poly(vinyl butyral)	20g

25

Thermographic Coating Solution:

The thermographic coating solution was prepared by adding 0.6g of methyl gallate, 0.2g of phthalazinone, 0.1g of succinimide, 0.1g of 2-imidazolidone, and 0.2g  
 30 of pyrogallol to 20g of the silver emulsion. The solution was coated onto a .08mm (3 mils) polyester substrate at a 0.1mm (4 mils) wet thickness and air dried at 21°C for 10 minutes.

An infrared-absorbing topcoat solution was  
 35 prepared by mixing 0.03g of Dye 6, 1.0g of CA 398-6 cellulose acetate resin, and 20.0g MEK. The topcoat solution was coated onto the thermographic layer at a

0.05mm (2 mils) wet thickness and air dried for 3 minutes at 60°C.

### Example 15

5        The following coating solutions were used in the preparation of Example 15:

Silver Emulsion:

10	Silver behenate homogenate (10% by weight in methyl ethyl ketone)	160g
	Butvar™ B-76 poly(vinyl butyral)	20g

### Thermographic Coating Solution:

15 The thermographic coating solution was prepared by adding 0.6g of methyl gallate, 0.1g of succinimide, 0.1g of 2-imidazolidone and 0.2g of L-ascorbic acid palmitate to 20g of the silver emulsion. The solution was coated onto a .08mm (3 mils) polyester substrate at 20 a 0.1mm (4 mils) wet thickness and air dried at 60°C for 3 minutes.

An infrared-absorbing topcoat solution was prepared by mixing 0.03g of Dye 6, 1.0g of CA 398-6 cellulose acetate resin, and 21.0g MEK. The topcoat solution was coated onto the thermographic layer at a 0.05mm (2 mils) wet thickness and air dried for 3 minutes at 60°C.

Table 3 summarizes the laser exposure results for each example. Maximum and minimum optical densities were measured using a MacBeth Model TD523 densitometer equipped with a status 18A filter.

### Table 3

Example	14	15
$D_{\max}$	3.73	2.73
$D_{\min}$	0.09	0.10

The radiation-absorbing dye may be incorporated primarily into the thermographic silver emulsion layer. It is believed that the thermographic silver emulsion layer is heated above its glass transition temperature, thereby allowing the reducing agent for silver ion to migrate to the light-insensitive organic silver salt (e.g., silver behenate) within the layer. The silver behenate is reduced by the reducing agent to elemental silver, forming a brown/black image. Toners are incorporated into the formulation to obtain a more neutral black color. The formation of the elemental silver in the imaged area not only provides UV opacity of the image in the final element, but also is an infrared-absorber which accelerates the image-forming process. The intensity of the infrared laser beam decreases exponentially as it penetrates into the thermographic silver emulsion layer. The thickness of the thermographic silver emulsion layer and the concentration of infrared dye will effect the sharpness of the image due to the decreasing intensity of the laser beam as a function of distance through the layer. The thickness of the thermographic silver emulsion layer is preferably between about 1 and 10 microns and more preferably, between about 2 and 6 microns. The concentration of the infrared dye and the thickness of the layer is adjusted such that the IR absorption of the layer is generally between 20% to 99%; preferably, 50 - 90%; and more preferably, 60 - 85%.

In high resolution imaging conditions, where the pixel dwell time is short and the laser peak intensity is high, ablation may occur if the infrared dye is incorporated solely in the thermographic emulsion layer of the construction. The heating rate is higher at the surface where the laser beam enters into the thermographic silver emulsion layer. As the elemental silver forms, the absorption of the laser beam

increases. This can cause the thermographic silver emulsion layer to overheat, thereby causing smoke, damage, or ablation.

By eliminating or decreasing the concentration of  
5 infrared dye in the thermographic silver emulsion layer  
and adding infrared dye in a layer adjacent to the  
thermographic silver emulsion layer, the penetration of  
the laser beam into the thermographic silver emulsion  
layer can be increased. The thermographic imaging  
10 element is exposed by directing the laser beam through  
the thermographic silver emulsion layer before striking  
the adjacent layer containing infrared dye. The  
infrared-absorbing layer can be positioned either above  
or below the thermographic silver emulsion layer  
15 relative to the substrate upon which the adjacent  
layers are deposited. The concentration of infrared  
dye in the infrared-absorbing layer is chosen such that  
the highest heating rate occurs at the interface  
between the infrared-absorbing layer and the  
20 thermographic silver emulsion layer. The concentration  
of infrared dye will depend upon the thickness of the  
thermographic layer and the physical properties of the  
dye. For example, the concentration of infrared dye in  
a 1 micron thick thermographic layer is adjusted to  
25 achieve an absorption of preferably about 90% or more.

During the course of an imaging laser pulse,  
elemental silver forms at this interface. The  
elemental silver formed increases the infrared  
absorption in this region of the thermographic silver  
30 emulsion layer and acts as a heat source for the image  
area within the thermographic silver emulsion layer.  
As the elemental silver density is built up adjacent to  
the infrared-absorbing layer, the intensity near the  
opposite surface of the thermographic silver emulsion  
35 layer is attenuated, thus reducing overheating in this  
region. The profile of the pixel image would resemble

an hour-glass shape, thus giving rise to a sharper image.

#### Example 16

This example demonstrates the effect of the thickness of the thermographic silver emulsion layer, the resin/silver ratio, the concentration of infrared dye, and the type of topcoat on the imaging characteristics of the inventive thermographic imaging element.

The following coating solutions are used in preparation of Samples A-P. X are variables specified in Table 4.

#### Silver Emulsion:

15	Silver behenate homogenate	160g
	(10% by weight in methyl ethyl ketone)	
	Butvar™ B-76 poly(vinyl butyral)	Xg

#### 20 Thermographic Coating Solution:

The thermographic coating solution was prepared by adding 15g of the silver emulsion to 0.8g of methyl gallate, 0.2g of succinimide, 0.1g of phthalazinone, 0.1g of 2-imidazolidone in 4mL of methanol and 1mL of methyl ethyl ketone. Before coating, Xg of Dye 2 was added to the solution. The solutions were coated onto a .08mm (3 mil) polyester substrate at X wet thickness and air dried at 70°C for 3 minutes.

A topcoat solution comprising a 2.4% by weight solution of CA398-6 cellulose acetate; Scripset™ 540 styrene-maleic anhydride copolymer available from Monsanto Company;; Tyril™ 880B styrene-acrylonitrile resin available from Dow Chemical Company, or poly(vinyl alcohol) (PVA), Airvol™ 523 available from Air Products and Chemicals, Inc., Allentown, PA and X% Dye 2 was overcoated onto the thermographic layer at X wet thickness and air dried at 50°C for 3 minutes.

Samples A-P were scanned with a laser sensitometer at several different scan speeds ranging from 20 to 60 cm/s. Density profiles of these lines at 415 nanometers were measured using a Perkin-Elmer microdensitometer PDS 1010M. Optical density measurements were taken at 826 nanometers (laser diode wavelength) and at 415 nanometers for the unimaged elements using a Shimadzu Spectrophotometer MPC-3100/UV3101PC.

Table 4

Sample #	A	B	C	D	E	F	G	H
Thermographic Layer thickness (wet, mm)	0.10	0.05	0.10	0.05	0.10	0.05	0.10	0.10
Top Coat Layer thickness (wet, mm)	0	0	0	0	0	0	0.05	0.05
Top Coat Resin Type	none	none	none	none	none	none	PVA	PVA
Butvar content in Silver Layer	20g	20g	10g	10g	5g	5g	0	0
Infrared Dye in Thermographic Layer	0.05g	0.05g	0.05g	0.05g	0.05g	0.05g	0	0.01g
Infrared Dye in Top Coat	0	0	0	0	0	0	0.10g	0.15g
Dmin (415nm)	0.95	0.14	1.1	0.3	1.24	0.75	0.34	0.53
Optical Density @ 825 nm	0.65	0.34	0.7	0.36	0.79	0.27	1.80	3.20

Sample #	I	J	K	L	M
Thermographic Layer thickness (wet, mm)	0.10	0.05	0.10	0.05	0.10
Top Coat Layer thickness (wet, mm)	0.05	0.05	0.05	0.05	0.05
Top Coat Resin Type	Cellulose Acetate	Cellulose Acetate	Cellulose Acetate	Cellulose Acetate	Tyri <sup>TM</sup>
Butvar content in Silver Layer	10g	10g	10g	10g	0

5	Infrared Dye in Thermographic Layer	0.07g	0.07g	0.10g	0.10g	0.05g
	Infrared Dye in Top Coat	0	0	0	0	0
	D <sub>min</sub> (415nm)	0.23	0.07	0.42	0.12	0.55
	Optical Density @ 825 nm	0.75	0.30	1.40	0.84	0.76

10	Sample #	N	O	P
	Thermographic Layer thickness (wet, mm)	0.10	0.10	0.10
	Top Coat Layer thickness (wet, mm)	0.05	0.05	0.05
15	Top Coat Resin Type	Scripset™	Scripset™	Scripset™
	Butvar content in Silver Layer	0	0	0
	Infrared Dye in Thermographic Layer	0.01g	0.01g	0
20	Infrared Dye in Top Coat	0.10g	0.15g	0.10g
	D <sub>min</sub> (415nm)	0.35	0.29	0.42
	Optical Density @ 825 nm	0.84	1.45	1.11

A laser sensitometer (1), shown in FIG. 1, was  
 used to evaluate the thermographic imaging elements in  
 Example 16. A 700 milliwatt beam (2) emitted from a  
 2361-P2 fiber coupled laser diode (3) (available from  
 Spectra Diode Labs) was focused onto a rotating drum  
 (4). The core diameter of the fiber (5) was 100  
 micrometers and the wavelength of the laser diode (3)  
 was 826 nanometers. The power on the rotating drum (4)  
 was 210 milliwatts and the spot shape was a flat-topped  
 cone with a spot size of 45 microns at full width half  
 maximum (FWHM). The flat-topped cone profile is  
 characterized by  $r_0$ , the radius of the peak intensity  
 of the cone, and  $r_1$ , the outer radius of the cone where  
 the intensity is nearly zero. A scanning slit beam

profiler was used to measure the intensity profile of the laser spot. Since the profiler integrates the intensity in the direction perpendicular to the slit movement, the actual spot profile was inferred from the profiler data. FIG. 2 shows a comparison of the profiler data (6) and the calculated profile data (7) expected for a flat-topped cone intensity profile with  $r_0$  equal to 10 micrometers and  $r_1$  equal to 36 micrometers. The curve was computed by integrating the model flat-topped cone intensity profile in one direction and rescaling.

As the intensity profile is scanned across the film, points lying under the spot profile will receive a finite exposure energy. This exposure energy is dependent upon the location of the point with respect to the scanned spot as well as the spot scan speed. FIG. 3a shows the total incident exposure energy plotted versus the distance across the beam in the cross/scan direction. The curve was calculated for the fiber-coupled sensitometer model beam shape, assuming a scan speed of 40 centimeters/seconds. In FIG. 3b, a microdensitometer profile of a line imaged with the energy profile shown in FIG. 3a, onto the thermographic element is shown. (Example 16, Sample N not shown.) The density data was collected using a narrowband filter at 415 nanometers. The density edges in FIG. 3b exhibit gradients that are larger than that of the incident exposure profile shown in FIG. 3a, indicating that the thermographic element (Example 16, Sample N not shown) has a high contrast.

The contrast of the thermographic element can be examined more quantitatively using a D-logE curve. A D-logE curve is a plot of the imaged film density versus the logarithm of the incident exposure energy. The theoretical form for this curve is given by  $D = \gamma \log (EE_F/E_0)$ ; where  $\gamma$  is equal to the slope of the D-



logE curve, E is equal to the incident exposure energy,  $E_f$  is equal to the fog or background level effective energy,  $E_0$  is equal to the minimum energy required to begin development of the image, and D is equal to the optical density of the element when exposed to exposure energy E. The background density is equal to  $\gamma \log E_f$ . Using the data shown in FIG. 3, a D-logE curve was computed and plotted in FIG. 4. From the model curve described by the optical density equation, the gamma or contrast of the element corresponds to the slope of the D-logE curve. The gamma value for the D-logE curve in FIG. 4 is 34. For a relative comparison, a typical rapid access wet-processed silver halide film has a gamma of approximately 10. The higher contrast is an advantage for graphic arts applications since high contrast halftone dots are desired for consistent tone curve control and also for new stochastic screening processes. Similar advantages apply to printed circuit board phototool applications.

The D-logE curve in FIG. 4 shows that the density development begins at approximately  $0.9 \text{ J/cm}^2$  and that density saturation at maximum density ( $D_{\max}$ ) occurs at  $1.2 \text{ J/cm}^2$ . It is to be understood that the optimum imaging speed and scanner exposure conditions will be unique for the particular scanner used to image the thermographic element.

Each of the samples described in Table 4 were scanned with the laser sensitometer (1) of FIG. 1 at several different scan speeds ranging from 20 to 60 centimeters/second. D-logE curves were calculated with a Perkin-Elmer microdensitometer using the data from the density profiles of these lines at 415 nanometers. The model parameters in the optical density equation described above were determined from the D-logE curves and are summarized below in Table 5.

Tabl 5

Sample#	A	B	C	D	E
Dmax (415 nm)			4.5		
5 mD Eo, 50	0.77	0.85	0.74	0.93	0.60
mD Esat, 50	1.30	1.40	1.40	1.80	1.23
mD Dmax, 50	3.50	3.50	3.65	3.50	3.60
mD Dmin, 50	0.85	0.40	0.55	0.65	0.80
gamma, 50	11.65	14.30	11.19	9.93	8.98
10 mD Eo, 100	0.966	0.94	0.96	1.00	1.03
mD Dsat, 100	1.27	1.30	1.26	10.00	1.32
mD Dmax, 100	3.5	3.0	3.4	0.0	3.6
mD Dmin, 100	0.80	0.35	0.80	0.00	0.80
gamma, 100	22.72	18.82	22.02	0.00	25.99
15 Gamma 100 /Gamma 50	1.95	1.32	1.97	0.00	2.89

Sample#	F	I	J	K	L
Dmax (415 nm)					
20 mD Eo, 50	0.65	0.80	1.13	0.56	0.35
mD Esat, 50	1.60	1.26	2.00	1.30	1.00
mD Dmax, 50	3.70	3.60	3.50	3.70	3.60
mD Dmin, 50	0.70	0.40	0.30	0.60	0.35
gamma, 50	7.80	16.22	12.90	8.47	7.12
25 mD Eo, 100	1.00	0.90	1.00	0.66	0.661
mD Dsat, 100	10.00	1.16	10.00	1.00	1.042
mD Dmax, 100	0.0	3.5	0.0	3.6	3.5
mD Dmin, 100	0.00	0.30	0.00	0.70	0.40
gamma, 100	0.00	29.03	0.00	16.07	15.88
30 Gamma 100 /Gamma 50	0.00	1.79	0.00	1.90	2.20

Sample#	N	O
Dmax (415 nm)	5.00	4.4
mD Eo, 50	0.95	0.88
mD Esat, 50	1.65	1.26
mD Dmax, 50	3.70	3.80
mD Dmin, 50	0.70	0.50
gamma, 50	12.51	21.16
mD Eo, 100	0.96	0.97
mD Dsat, 100	1.20	1.26
mD Dmax, 100	3.7	3.8
mD Dmin, 100	0.40	0.50
gamma, 100	34.05	29.05
Gamma 100 /Gamma 50	2.72	1.37

15

mD Eo,50 = Eo value from D-logE curve, scan speed at 20 centimeters/second (cm/s)

mD Esat,50 = Esat value from D-logE curve, scan speed at 20 cm/s

mD Dmax,50 = Maximum Density at 20 cm/s

mD Dmin,50 = Minimum Density at 20 cm/s

20

gamma,50 = gamma value when scanning at 20 cm/s

mD Eo,100 = Eo value from D-logE curve, scan speed at 40 cm/s

mD Esat,100 = Esat value from D-logE curve, scan speed at 40 cm/s

mD Dmax,100 = Maximum Density at 40 cm/s

mD Dmin,100 = Minimum Density at 40 cm/s

25

gamma,100 = gamma value when scanning 40 cm/s

gamma 100/gamma 50 = (gamma at 40 cm/s) divided by (gamma at 20 cm/s)

The average value Eo for samples A through L is  $0.8 \pm 0.2$  Joules/cm<sup>2</sup> at a scan speed of 20 cm/s and  $0.9 \pm 0.2$  Joules/cm<sup>2</sup> at a scan speed of 40 cm/s. The minimum exposure energy required to begin density development is relatively independent of the scan speed. The Esat values are independent of speed as well. The average value for Esat is  $1.3 \pm 0.2$  Joules/cm<sup>2</sup> at a scan speed of 20 cm/s and  $1.2 \pm 0.1$  Joules/cm<sup>2</sup> at a scan speed of 40 cm/s. The gamma values show evidence of imaging performance differences at the two speeds. The average gamma value for Samples A through L at a scan speed of 20 cm/s is  $12 \pm 4$  while

the average gamma value at 40 cm/s is  $24 \pm 6$ . Thus, the gamma values appear to increase significantly as the scan speed is increased. It is possible that at the lower scan speeds the heat diffusion is more significant giving rise to loss of sharpness of the edges and thus, reducing the gamma of the image. Unlike photothermographic silver media, thermographic silver elements show a more pronounced effect of exposure conditions.

Samples C, I, and K were coated with different infrared dye concentrations. Samples C and I have an 80% absorption at the laser diode wavelength of 826 nanometers. Sample K was coated to the same thickness, but was loaded with more infrared dye so that it absorbs 96% at 826 nanometers. The average  $E_o$  and  $E_{sat}$  values for C and I are 0.93 Joules/cm<sup>2</sup> and 1.21 Joules/cm<sup>2</sup>, respectively, at a scan rate of 40 cm/s. The  $E_o$  and  $E_{sat}$  values for Sample K are 0.66 Joules/cm<sup>2</sup> and 1.0 Joules/cm<sup>2</sup>, respectively. The sensitivity of the film appears to be slightly improved by the 16% increase in the layer absorption.

The effect is more pronounced for thinner coatings. Samples D, J, and L were coated at half the thickness of C, I, and K. Samples D and J absorb only about 50% of the incident laser radiation, and do not image at the 40 cm/s scan rate. Sample L absorbed 85% of the incident laser radiation. The average  $E_o$  and  $E_{sat}$  values for D and J are 1.0 Joules/cm<sup>2</sup> and 1.9 Joules/cm<sup>2</sup>, respectively at 20 cm/s, whereas the  $E_o$  and  $E_{sat}$  values for Sample L are 0.35 Joules/cm<sup>2</sup> and 1.0 Joules/cm<sup>2</sup>, respectively. The exposure energy values for L are lower than that of D and J. Sensitivity is enhanced with increasing laser absorption in the thermographic silver emulsion layer, or with increasing infrared dye concentration. The edges of the imaged lines scanned at 40 cm/s in Samples K and L were

smoother than the other single infrared layer samples. The line edge sharpness can be improved by increasing the infrared dye concentration in the layer.

A comparison of samples with different  
5 thicknesses, but similar absorption percentages, indicates that a thinner coating with a higher infrared dye concentration is more sensitive than one with a thicker coating. The  $E_o$  and  $E_{sat}$  values for K are 0.56 and 1.3 Joules/cm<sup>2</sup>, respectively, at 20 cm/s, whereas  
10 the  $E_o$  and  $E_{sat}$  values for L are 0.35 and 1.0 Joules/cm<sup>2</sup>, respectively. The thickness of Sample L is half that of K, but it absorbs 85% of the laser radiation, which is roughly comparable to that of K. Increasing the infrared dye concentration may cause  
15 ablation due to increased peak temperatures in the thermographic layer. The sensitivity of a single thermographic silver emulsion layer containing infrared dye can be maximized by coating the thermographic silver emulsion layer as thin as possible with the  
20 highest achievable infrared dye concentration, while maintaining the desired maximum density.

The quality of the imaged line is affected by the resin to silver ratio. The exposure energy values and the gamma values are not significantly affected by  
25 changes in the resin to silver ratio, as shown in Table 5 for Samples A, C, and E. However, the micrographs of these samples indicate that the resin to silver ratio does affect the image quality of the lines. As the resin to silver ratio is decreased, the edges of the  
30 lines become rough and jagged, and the density uniformity across and along the imaged line decreases. Decreasing the resin concentration should enhance the sensitivity of the material due to less bulk material to heat. However, the jagged edges appear to have  
35 offset this advantage. The resin to silver ratio is preferably between about 25 - 50 wt%.

Another embodiment of the present invention comprises the addition of infrared dye in a layer adjacent to the thermographic silver emulsion layer. Samples N, O, G, H, and P in Example 16 evaluate the addition of an infrared dye in the topcoat of a thermographic element. For some unknown reason, Samples M, G, and H imaged poorly and therefore, are not included in Table 4. Samples N, O, and P exhibited improved line quality compared to the samples containing infrared dye in the thermographic layer only. The thermographic silver layers in Samples N, O, and P were overcoated with a .05 millimeter coating of Scripset™ resin that contains a high concentration of infrared dye. A piece of pressure-sensitive adhesive tape was used to separate the topcoat from the thermographic silver emulsion layer to verify that the two layers had not intermixed. Samples N and O have gamma values greater than 34 and 30, respectively, at a scan speed of 40 cm/s. These gamma values are comparable to a conventional silver halide duplication film. For comparison, a typical rapid access silver halide film has a gamma of approximately 10. The quality of Sample P is similar to N and O, although a D-log E curve was not computed for this sample. Both N and O exhibit sharp smooth line edges with an approximate 1 micron edge roughness. The samples containing infrared dye in the thermographic silver layer only had rougher edges than Samples N and O. The density uniformity of Samples N, O, and P were within  $\pm 5\%$ . The sensitivity of Samples N and O are comparable to the samples having no topcoat containing infrared dye. No ablation was observed in Samples N, O and P. Improved edge contrast, edge sharpness, and density uniformity can be achieved by the addition of infrared dye in a layer adjacent to the thermographic silver layer. In addition, the susceptibility to ablation is

also reduced in this construction. The concentration of the infrared dye in the thermographic silver layer is in an amount such that the absorption of the laser radiation in the thermographic layer is preferably less than or equal to 40% and more preferably, less than or equal to 35%.

FIG. 5 shows the imaged (8) and non-imaged (background) (9) transmission spectra for Example 16, Sample N. The enhanced infrared dye absorption peak at 820 nanometers is clearly evident. The density at the laser diode wavelength of 826 nanometers increases from 0.84 (14.5% transmission) to 1.26 (5.5% transmission), while the density at 415 nanometers increases from 0.355 (44.2% transmission) to 5.0 (nearly 0% transmission). The elemental silver formed in the thermographic layer during exposure provides an enhanced absorption difference in the ultraviolet (UV), which is an advantage in UV mask applications. In Table 5, the  $D_{\max}$  measured by the microdensitometer was 3.7 which is lower than the value obtained from the spectrophotometer. Apparently, the maximum optical density that can be measured by the microdensitometer is limited to about 3.7. This implies that many of the gamma values computed in Table 5 are lower than the true values and therefore, should be treated as conservative estimates.

In order to compare the imaging characteristics of the thermographic elements with little or no effects due to heat dissipation, Examples 1, 2, 3, 4, 5, 6 and 16 (Sample N) were imaged using a 150 milliwatt (110 milliwatts at the image plane) laser diode (SDL-5422, available from Spectra Diode Labs) emitting at 811 nanometers. The beam was focused to an 8 micrometer spot size (full width at  $1/e^2$  level) and scanned at 213 centimeters/second with a 4.5 micrometer cross scan

line spacing. Table 6 summarizes the results from this evaluation.

Table 6

Example	Dmax, 365nm	Dmin, 365nm	Dmax- Dmin, 365nm	Dmax, 415nm	Dmin, 415nm	Dmax- Dmin, 415nm
1	2.17	0.31	1.85	2.48	0.25	2.23
2	2.58	0.39	2.19	2.94	0.29	2.65
3	1.78	0.39	1.39	1.85	0.29	1.56
4	3.05	0.63	2.42	3.13	0.57	2.56
5	4.50	0.57	3.93	5.00	0.42	4.58
6	4.04	0.90	3.14	5.00	0.59	4.01
16, Sample N	4.40	0.47	3.92	5.00	0.53	4.46

The data shows that the higher contrast (Dmax-Dmin) films are achieved when silver laurate is used in combination with barbituric acid in the thermographic silver emulsion layer (Examples 5 and 6) or a higher concentration of methyl gallate is used in the silver behenate formulation (Example 16, Sample N). In order to provide workable UV contract applications, the contrast is preferably greater than about 2.50. The data also shows that the addition of benzotriazole inhibits the speed of the film; however, the decrease in speed is minimized when silver laurate is used for the silver soap. Even though a slight decrease in speed may be observed, the improved light stability, as shown in Table 1, provides an advantage for including benzotriazole in the thermographic silver emulsion.

Reasonable variations and modifications are possible from the foregoing disclosure without departing from either the spirit or scope of the present invention as defined in the claims.



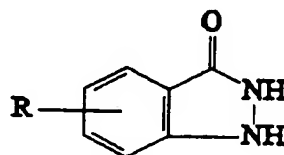
What is Claimed is:

1. A thermographic imaging element comprising a substrate having coated on at least one surface thereof  
5 a thermographic imaging system comprising at least one layer comprising light-insensitive organic silver salt; reducing agent for silver ion; binder; toner; and a dye which absorbs radiation in the wavelength range of 750-1100 nm, wherein said at least one layer comprising  
10 said light-insensitive organic silver salt forms an image density greater than about 1.0 when exposed to 0.10 - 2.0 joules/cm<sup>2</sup> of said radiation in 0.20 to 200 microseconds.
- 15 2. The element of Claim 1 wherein said image density is greater than about 2.00 and comprises metallic silver.
3. The element of Claim 1 when said image density is  
20 greater than about 2.50 and comprises metallic silver.
4. The element of Claim 1 wherein said image density is greaater than about 2.75 and comprises metallic silver.
- 25 5. The element of Claim 1 wherein said dye absorbs radiation in the wavelength range of about 750 to 900 nm.
- 30 6. The element of Claim 1 wherein said thermographic imaging system further comprises a development accelerator.
7. The element of Claim 1 where said light-  
35 insensitive organic silver salt is a silver salt of a carboxylic acid containing 10-30 carbon atoms.

8. The element of Claim 7 where said silver salt is silver benate or silver laurate.

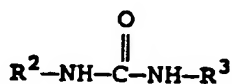
9. The element of Claim 6 wherein said development accelerator is one selected from the group consisting of:

(i) a 3-indazolinone compound of the formula:



wherein: R is selected from the group consisting: of hydrogen; an alkyl group of 1 to 4 carbon atoms; halogen; -COOH; and  $R^1\text{COOH}$  wherein  $R^1$  is an alkyl group of 1 to 4 carbon atoms; and

(ii) a urea compound of the formula:



wherein:  $R^2$  and  $R^3$  each independently represent hydrogen; a  $C_1$  to  $C_{10}$  alkyl or cycloalkyl group; or phenyl; or  $R^2$  and  $R^3$  together form a heterocyclic group containing up to 6 ring atoms.

10. The element of Claim 9 wherein R represents hydrogen;  $R^2$  and  $R^3$  each independently represent a  $C_1$  to  $C_5$  alkyl or cycloalkyl group; or phenyl; or  $R^2$  and  $R^3$  together form a heterocyclic group containing up to 5 ring atoms.

11. The element of Claim 1 wherein said toner is at least one selected from the group consisting of phthalazinone, phthalazine, barbituric acid, succinimide, and pthalimide.

5

12. A thermographic imaging element comprising a substrate coated with a thermographic imaging system, said thermographic imaging system comprising at least two adjacent layers, one of said adjacent layers  
10 comprising light-insensitive organic silver salt; reducing agent for silver ion; toner; binder; and optionally, a dye which absorbs radiation having a wavelength in the range of about 750-1100 nm; and said  
15 other adjacent layer consisting essentially of binder and said dye which absorbs radiation in the wavelength range of about 750-1100 nm, wherein said layer comprising said light-insensitive organic silver salt forms an image density of greater than about 1.0 when  
20 exposed to 0.10 - 2.0 joules/cm<sup>2</sup> of said radiation in 0.20 to 200 microseconds.

13. The element according to Claim 12 wherein said light-insensitive organic silver salt is a silver salt of a carboxylic acid containing 10-30 carbon atoms.

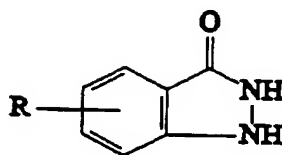
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14. The element according to Claim 12 wherein said silver salt of a carboxylic acid is silver behenate or silver laurate.

30 15. The element according to Claim 12 wherein said thermographic imaging system further comprises a development accelerator.

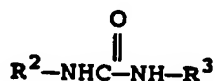
16. The element according to Claim 15 wherein said  
35 development accelerator is selected from the group consisting of:

(i) a 3-indazolinone compound of the formula:



10

wherein: R is selected from the group consisting of hydrogen; an alkyl group of 1 to 4 carbon atoms; halogen; -COOH; and  $R^1\text{COOH}$  wherein  $R^1$  is an alkyl group of 1 to 4 carbon atoms; and  
 15 (ii) a urea compound of the formula:



wherein:  $R^2$  and  $R^3$  each independently represent hydrogen; a  $C_1$  to  $C_{10}$  alkyl or cycloalkyl group; or phenyl; or  $R^2$  and  $R^3$  together form a heterocyclic group containing up to 6 ring atoms.  
 25

17. The element according to Claim 16 wherein R represents hydrogen;  $R^2$  and  $R^3$  each independently  
 30 represent a  $C_1$  to  $C_5$  alkyl or cycloalkyl group; or phenyl; or  $R^2$  and  $R^3$  together form a heterocyclic group containing up to 5 ring atoms.

18. The element according to Claim 12 wherein said dye  
 35 absorbs radiation having a wavelength in the range of from about 750 to 900 nm.

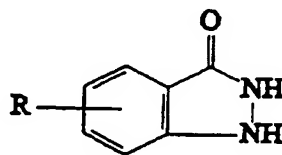
19. The element according to Claim 12 wherein said image density is greater than about 2.00 and comprises metallic silver.
- 5 20. The element according to Claim 12 wherein said image density is greater than about 2.50 and comprises metallic silver.
21. The element according to Claim 12 wherein said  
10 image density is greater than about 2.75 and comprises metallic silver.
22. The element according to Claim 12 wherein said toner is at least one selected from the group  
15 consisting of phthalazinone, phthalazine, barbituric acid, succinimide, and phthalimide.
23. A process for forming an image comprising the step of exposing a thermographic imaging element comprising  
20 a substrate coated with a thermographic imaging system, said thermographic imaging system comprising at least one layer comprising light-insensitive organic silver salt; reducing agent for silver ion; a dye which absorbs radiation in the wavelength range of about 750-  
25 1100 nm; toner; and binder, to radiation having a wavelength in the range of about 750-1100 nm wherein said at least one layer comprising said light-insensitive organic silver salt forms an image density of greater than about 1.0 when exposed to 0.10 - 2.0  
30 joules/cm<sup>2</sup> of said radiation in 0.20 - 200 microseconds.
24. The process according to Claim 23 wherein said light-insensitive organic silver salt is a silver salt  
35 of a carboxylic acid containing 10-30 carbon atoms.

25. The process according to Claim 24 where in said silver salt of a carboxylic acid is silver behenate or silver laurate.

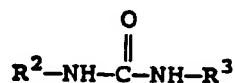
5 26. The process according to Claim 23 wherein said thermographic imaging system further comprises a development accelerator.

27. The process according to Claim 26 wherein said  
10 development accelerator is selected from the group consisting of:

(i) a 3-indazolinone compound of the formula:



wherein: R is selected from the group consisting of hydrogen; an alkyl group of 1 to 4 carbon atoms; halogen; -COOH; and  $R^1\text{COOH}$  wherein  $R^1$  is an  
25 alkyl group of 1 to 4 carbon atoms; and  
(ii) a urea compound of the formula:



wherein:  $R^2$  and  $R^3$  each independently represent hydrogen; a  $C_1$  to  $C_{10}$  alkyl or cycloalkyl group; or phenyl; or  $R^2$  and  $R^3$  together form a heterocyclic group containing up to 6 ring atoms.

28. The process according to Claim 27 wherein R represents hydrogen; R<sup>2</sup> and R<sup>3</sup> each independently represent a C<sub>1</sub> to C<sub>5</sub> alkyl or cycloalkyl group; or phenyl; or R<sup>2</sup> and R<sup>3</sup> together form a heterocyclic group containing up to 5 ring atoms.

29. The process according to Claim 23 wherein said dye absorbs radiation having a wavelength in the range of from about 750 to 900 nm.

10

30. The process according to Claim 23 wherein said image density is greater than about 2.0 and comprises metallic silver.

15 31. The process according to Claim 23 wherein said image density is greater than about 2.50 and comprises metallic silver.

32. The process according to Claim 23 wherein said  
20 image density is greater than about 2.75 and comprises metallic silver.

33. The process according to Claim 23 wherein said  
25 toner is at least one selected from the group consisting of phthalazinone, phthalazine, barbituric acid, succinimide, and phthalimide.

34. A process for forming an image comprising the step  
30 of exposing a thermographic imaging element comprising a substrate coated with a thermographic imaging system, said thermographic imaging system comprising at least two adjacent layers, one of said adjacent layers comprising light-insensitive organic silver salt; reducing agent for silver ion; toner; binder; and  
35 optionally, a dye which absorbs radiation having a wavelength in the range of about 750-1100 nm and said

other adjacent layer consisting essentially of binder and said dye which absorbs radiation in the wavelength range of about 750-1100 nm, to radiation having a wavelength range of about 750-1100 nm which is directed  
5 to said thermographic imaging element through said layer comprising said light-insensitive organic silver salt before striking said adjacent layer consisting essentially of binder and said dye which absorbs radiation such that said layer comprising said light-  
10 insensitive organic silver salt forms an image density of greater than about 1.0 when exposed to 0.10 - 2.0 joules/cm<sup>2</sup> of said radiation in 0.20 to 200 microseconds.

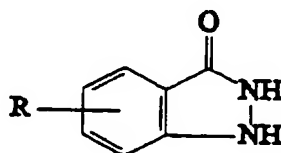
15 35. The process according to Claim 34 wherein said light-insensitive organic silver salt is a silver salt of a carboxylic acid containing 10-30 carbon atoms.

36. The process according to Claim 34 wherein said  
20 silver salt of a carboxylic acid is silver behenate or silver laurate.

37. The process according to Claim 34 wherein said thermographic imaging system further comprises a  
25 development accelerator.

38. The process according to Claim 37 wherein said development accelerator is selected from the group consisting of:

30 (1) a 3-indazolinone compound of the formula:



35



- wherein: R is selected from the group consisting of hydrogen; an alkyl group of 1 to 4 carbon atoms; halogen; -COOH; and R<sup>1</sup>COOH wherein R<sup>1</sup> is an alkyl group of 1 to 4 carbon atoms; and
- (ii) a urea compound of the formula:



- wherein: R<sup>2</sup> and R<sup>3</sup> each independently represent hydrogen; a C<sub>1</sub> to C<sub>10</sub> alkyl or cycloalkyl group; or phenyl; or R<sup>2</sup> and R<sup>3</sup> together form a heterocyclic group containing up to 6 ring atoms.

39. The process according to Claim 38 wherein R represents hydrogen; R<sup>2</sup> and R<sup>3</sup> each independently represent a C<sub>1</sub> to C<sub>5</sub> alkyl or cycloalkyl group; or phenyl; or R<sup>2</sup> and R<sup>3</sup> together form a heterocyclic group containing up to 5 ring atoms.

40. The process according to Claim 34 wherein said dye absorbs radiation having a wavelength in the range of from about 750 to 900 nm.

41. The process according to Claim 34 wherein said image density is greater than about 2.00 and comprises metallic silver.

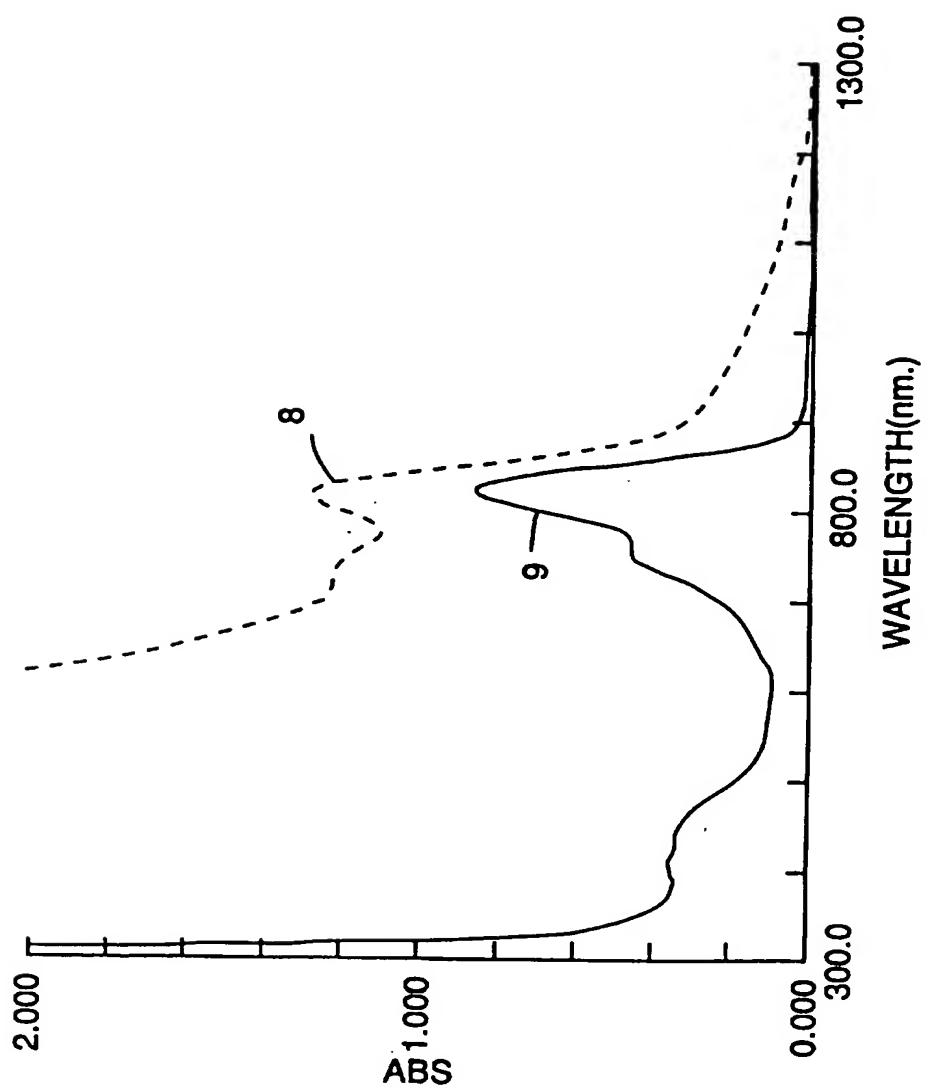
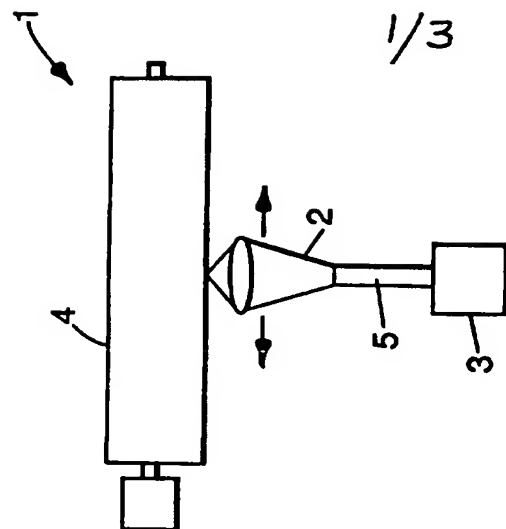
42. The process according to Claim 34 wherein said image density is greater than about 2.50 and comprises metallic silver.

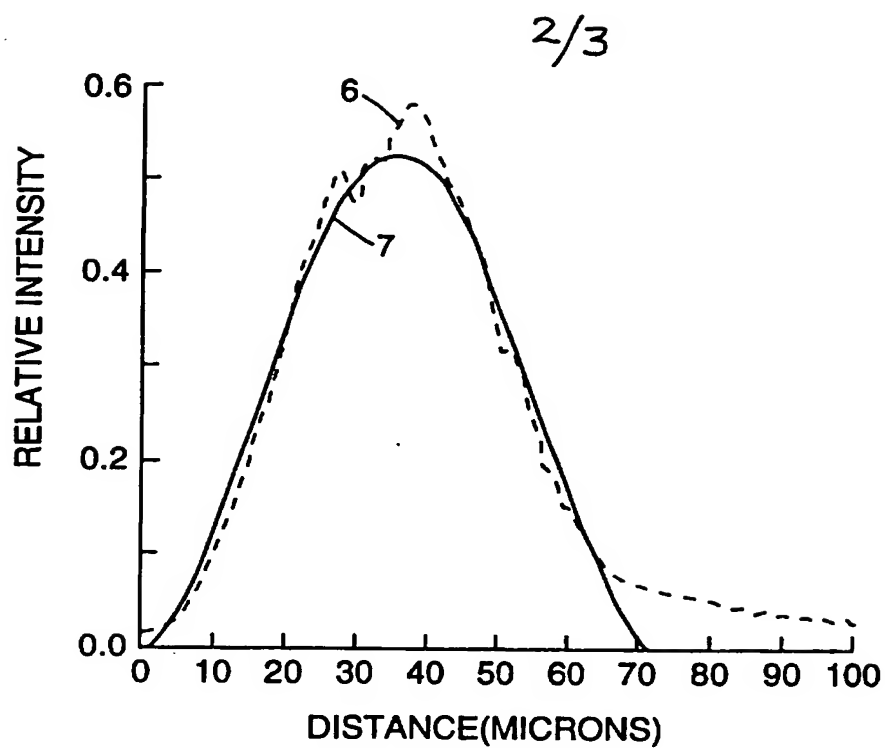
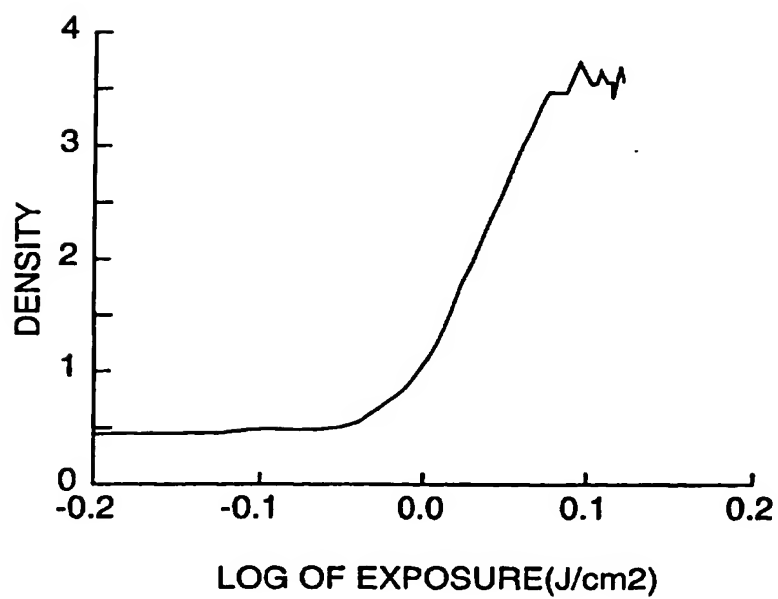
43. The process according to Claim 34 wherein said image density is greater than about 2.75.

44. The process according to Claim 34 wherein said t ner is at least one selected from the group consisting of phthalazinone, phthalazine, barbituric acid, succinimide and pthalimide.

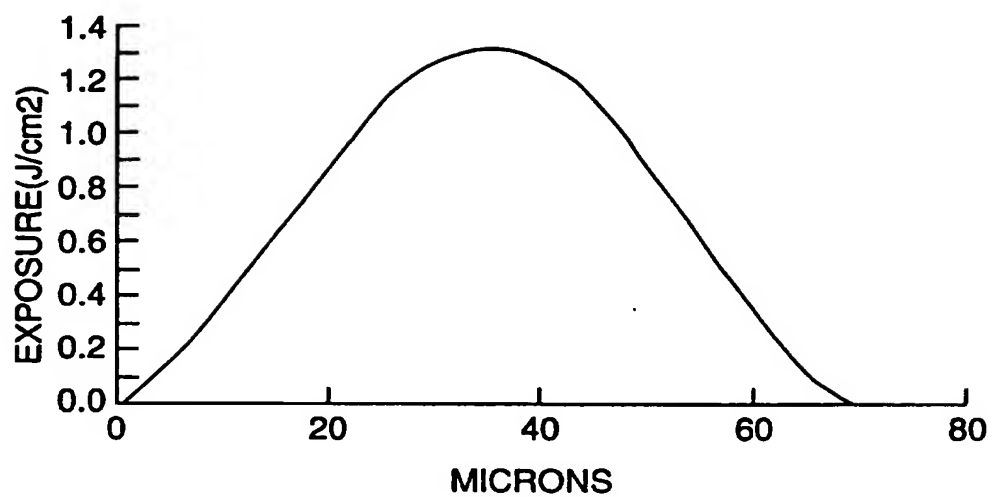
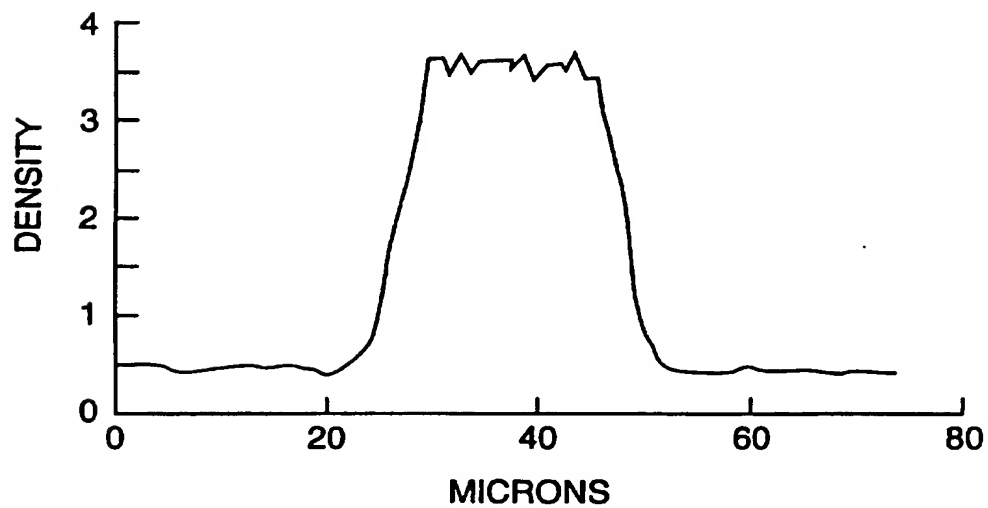
5

45. The process according to Claim 34 wherein said dye which absorbs radiation having a wavelength of from about 750-1100 nm is present in both adjacent layers.



**FIG. 2****FIG 4**

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**FIG.3a****FIG 3b**

# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 95/09659

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 G03C1/498

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 582 144 (3M) 9 February 1994 see page 3, line 7 - line 12 see page 3, line 35 - page 6, line 33 see page 7, line 25 - line 38 see page 10, line 23 - line 27 -----	1-45

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search

19 September 1995

Date of mailing of the international search report

- 2. 10. 95

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### Information on patent family members

**PCT/US 95/09659**

Form PCT/ISA/218 (patent family annex) (July 1992)

